WORKSHOPS

Using Powder Data to Solve Crystal Structures

David Cox
Peter Stephens
(SUNY @ Stony Brook)

This workshop, held on May 18, 1998 at the Annual NSLS Users' Meeting, was motivated by the recent rapid advances in the application of powder diffraction techniques to the *ab initio* solution of unknown structures. In contrast to the well-known Rietveld method for structure refinement, this is a relatively new application which has been driven mainly by the development of high-resolution synchrotron x-ray techniques, especially for framework structures such as zeolites, fullerene derivatives and other molecular compounds, and small organic molecules of pharmaceutical significance. The roughly 80 attendees were treated to a state-of-the-art exposition by an international cast of speakers from the USA and Europe, where much of the cutting-edge work in this field is currently taking place.

After Henk Schenk (U. of Amsterdam) started the proceedings with an introduction to the use of direct methods for structure solution from powder data, zeolites took center stage with talks by Lynne McCusker (ETH, Zurich) about her structural "toolbox" and two new tools for solving zeolite structures, texture and structure envelopes, and Ralf Grosse-Kunstleve (Yale U.) on a third new tool, which allows useful crystal chemical information to be incorporated via Fourier recycling and a search for unique topologies (the "FOCUS" method). John Newsam (Molecular Simulations Corp.) described some successful approaches to structure determination based on model construction and simulated annealing, and Dick Harlow (DuPont Corp.) closed out the morning session with an update on the $1000 "DuPont Challenge", to be awarded to the first person to solve the structure of $HAlF_4$ (an intermediate product in the industrial synthesis of AlF_3 catalysts) from powder data collected at the NSLS. No winner has yet been announced!

Molecular and organic compounds were the focus of the afternoon talks, led off by Ken Shankland (Rutherford Appleton Lab.) with a description of real-space techniques that are suitable for organic molecules, including examples of structures solved by simulated annealing and genetic algorithms. Jim Kaduk (Amoco Corp.) discussed the structure solution of several moderately large organic molecules using more conventional techniques, while Robert Dinnebier (U. of Bayreuth) compared standard tools (such as direct methods) and some unconventional algorithms, including extended use of chemical constraints and rigid bodies, grid searches, and the use of pseudo-atoms for compact units such as phenyl rings to a variety of structure solutions.

Peter Stephens (SUNY, Stony Brook) discussed several aspects of lineshape modelling, including a newly-developed algorithm for handling anisotropic broadening due to lattice strains, and in the final talk, Bob Von Dreele (Los Alamos National Lab.) described some first attempts at protein crystallography with powder samples, in which with appropriate constraints he was able to refine the structure of whale myoglobin (1401 atoms in a 65,000 Å 3 unit cell!) from high-resolution data taken at the NSLS.

On this impressive note, Peter Stephens closed the meeting by urging the audience to make more use of the several high-resolution synchrotron powder instruments available, and to apply these powerful new tools for *ab initio* structure solution to more complex materials of scientific and commercial interest.

The success of the workshop was in no small part due to the support of the following sponsors whose generosity is gratefully acknowledged: the International Centre for Diffraction Data, Air Products, Amoco, Chevron, Clariant, Mobil, UOP, SUNY X3B1 Powder Diffraction Facility, X7A PRT. ■

WORKSHOPS

In Situ Surface Manipulation

Ian Robinson
(University of Illinois @ Urbana)

A workshop on *in situ* manipulation of surfaces using X-Ray diffraction methods was held in conjunction with the Annual NSLS Users' Meeting on Wednesday, May 20, 1998 from 9:00am to 5:30pm. The workshop's emphasis was the structure and properties of surfaces and interfaces in their working environments. An exciting and stimulating series of talks was presented, covering a wide range of physics, chemistry and materials topics that have been addressed by experiments at NSLS. Valuable support for the meeting came from the Users' Executive Committee. The attendance varied from 25 to 50 as participants selected parts of the program of interest to them.

Bill Elliot from the University of Missouri spoke about growth morphology of Ag during homoepitaxy, where he reported roughness exponents at different growth temperatures. Hubert Zajonz from the BNL Physics Department and Odile Robach of the University of Illinois compared their heteroepitaxial deposition systems, Cu on Ru(0001) and Ni on Ag(001). New and unique unit-cell structures are stabilized by epitaxial forces in the thin-film state.

Joel Brock of Cornell University presented his new results on the nucleation and ordering kinetics of Cu films electrochemically deposited on Pt(111). His group used a periodic drive of the applied potential to attain good statistics with excellent temporal resolution. Mary Ryan and Jia Wang of the BNL Department of Applied Science then presented their respective structural studies of the passive oxide film formed on iron and the Tl-Br coadsorbate on Au(111). In both cases, the chemical complexity of these highly relevant compound systems was impressive, and structural details down to the oxygen site occupation and the Au displacements were discovered.

After an outdoor barbecue lunch, Ken Evans-Lutterodt of Lucent Technologies talked about a new kind of order detected in very thin SiO_2 layers on Si, an interface of great importance to the semiconductor industry. A discussion broke out concerning the different aspects of structure probed by reflectivity and truncation rod measurements. This theme was developed further by Pulak Dutta of Northwestern University who spoke about self-assembled and Langmuir monolayers on Si substrates. Elaine DiMasi of BNL Physics followed with animated results of surface segregation in liquid Hg alloys, which showed very different temperature dependence from pure Hg. Then Mike Bedzyk, also of Northwestern University, introduced the standing-wave technique with its *in situ* applications to the interface between calcite and water.

Art Baddorf of ORNL introduced his original ideas about dynamic Smoluchowski smoothing of surfaces and its coupling to surface vibrations. High-frequency optic modes lead to transient structures containing paired atoms (just like in a reconstruction) whose electronic response drives a bigger relaxation than in ideal non-vibrating surfaces. The final speaker of the day was Joe Woicik of NIST, who captured some overflow audience from the already closed EXAFS workshop for his presentation on EXAFS and diffraction determinations of InGaAs interatomic spacings. ■

Crystallography Under High Pressure: Techniques for Everyone

Jiuhua Chen
(SUNY @ Stony Brook)

Synchrotron radiation has greatly benefited high pressure research. A high pressure apparatus has either a very small amount of sample or a large amount of pressure medium surrounding the sample; therefore, *in situ* high pressure studies with x-rays have a great demand for synchrotron radiation. This workshop was held on May 20, 1998, in conjunction with the NSLS Users' Meeting and co-sponsored by the Center for High Pressure Research (CHiPR). In this one-day workshop, the most recent technological developments and scientific research with synchrotron radiation under high pressure were reviewed. Ten invited speakers presented the latest high pressure techniques and research at the NSLS, APS, ESRF, SPring-8 and PF.

After a brief introduction by Jiuhua Chen (workshop organizer, SUNY at Stony Brook), Donald Weidner (Director, CHiPR, SUNY at Stony Brook) and Russell Hemeley (CHiPR, Carnegie Institute at Washington) reviewed the research activities of the large-volume press (LVP) and the diamond anvil cell (DAC) at the NSLS, respectively. Many pioneer developments of methodology and technology for LVP and DAC, such as rheological measurement, uniform laser heating and translating imaging plate system, were presented. A comprehensive HP system including both LVP and DAC is emerging at the NSLS. The studies have a very important impact in understanding the interior of the earth as well as some other aspects of physics and material science.

In the late morning session, two special topic talks on ultrasonic measurement of sound velocities with LVP and x-ray spectroscopy with DAC were given by Robert C. Liebermann (CHiPR, SUNY at Stony Brook) and Jean-Pascal Rueff (NSLS). A simultaneous measurement of ultrasonic sound velocity and x-ray diffraction has been achieved for the first time at the X17B1 beamline. This development opens new opportunities for establishing absolute pressure scales. Spectroscopic techniques, including inelastic scattering, x-ray absorption and emission, with a Be-gasket DAC provide valuable information for understanding the electronic structures of materials under high pressure. A general discussion on Rietveld refinement with energy dispersive powder diffraction data using synchrotron radiation light source, as well as a neutron "heavy" source, was given by Robert B. Von Dreele (Los Alamos National Laboratory), and some pioneer trials of LaBeil fit and Rietveld fit for high-pressure diffraction data collected at the NSLS were also discussed.

The afternoon sessions focused on the reports of high pressure research from the third-generation synchrotron radiation facilities. Francesco Sette (ESRF) presented the development of inelastic x-ray scattering measurements in the ~20 KeV energy region with energy resolutions tunable in 1.5 - 7 meV range. This technique overcomes the kinematic limitations of the traditional neutron inelastic scattering system and favors high-pressure experiments with small samples. An overview of the high pressure research at the ESRF was given by Daniel Hausermann. The high pressure cell has been a widely accessed tool at the ESRF. In the past year, about one third of the over 20 optimized beamlines have been used to carry out the high pressure experiments. The 12-second cycle "Fastscan" imaging plate detector enhanced the capabilities of LVP and laser-heating DAC. Combining an IP detector and a background-subtraction technique, which was initiated at CHiPR, reaction and synthesis kinetics was studied using the LVP. Osamu

Shimomura (SPring-8) introduced the recent high pressure research in Japan (both Photon Factory and SPring-8). The result of spinel - perovskite+perclase phase boundary study using the double-stage large-volume apparatus, SPEED1500, was published as the first research paper of the SPring-8 facility. The press offers the highest pressure so far reached in an LVP in conjunction with synchrotron radiation.

The high-pressure research at GeoSoilEnviroCARS was reviewed by Yanbin Wang (APS). Both the DAC and LVP systems at the APS have been complemented based on the success of CHiPR at the NSLS. HPCAT is a proposed integrated high-pressure facility at the APS. David Mao (CHiPR, Carnegie Institute at Washington) described the beamline design which will integrate the well established HP x-ray diffraction programs and the new frontiers in HP x-ray spectroscopy. ■

Biological and Environmental Applications

Barbara Illman
(University of Wisconsin)

Biological and environmental sciences are increasingly using synchrotron techniques in diverse areas of research. A workshop on biology and environmental applications was held on May 18, 1998 in conjunction with the 1998 Annual NSLS Users' Meeting. This workshop included research conducted on a variety of X-ray and VUV beamlines at NSLS. Speakers discussed current and future developments in X-ray computed microtomography, EXAFS, microXANES, STXM, soft x-ray microscopy, fluorescence spectroscopy, and x-ray crystallography for studies in molecular and developmental biology, human pathology, bioremediation of toxic wastes, impact of toxins on ecosystem dynamics, plant pathology, and forest ecology. James Penner-Hahn (U. of Michigan) presented research on spatial and temporal imaging of Zn speciation during development of fish eggs using microXANES. Paul Bertsch (U. of Georgia) presented research on the distribution and chemical speciation of metals and metalloids in environmental samples by micro X-ray fluorescence and micro X-ray absorption spectroscopies. Mark Chance (Albert Einstein Coll. of Med.) described the use of synchrotron X-radiation for studies on the structural biology of RNA folding. Cathryn Lawson (BNL Biology) told of protein crystallography to unlock the secrets of the tick-borne pathogen that causes lime disease. Don Huber (Purdue U.) told how microXANES was used in monitoring oxidative reactions to determine basic mechanisms of plant pathogenesis. Ulrich Neuhaeusler (SUNY at Stony Brook) summarized the soft X-ray spectromicroscopy research at X1A, including studies of hydrated colloidal systems. Formation of a PRT for the recently developed X-ray microtomography beamline at NSLS was described by Barbara Illman (U. of Wisconsin, Forest Products Laboratory). Two speakers gave talks for this workshop and for the workshop on Applications of Infrared Synchrotron Radiation. George Flynn questioned the potential of organic-carbon-based molecules on extraterrestrial samples using FTIR and STXM measurements. Lisa Miller (Albert Einstein Coll. of Med.) presented applications of synchrotron infrared microspectroscopy to the study of biological cells and tissues. The talks in this workshop represented synchrotron-based research that is making an impact on the biological and environmental sciences. ■

WORKSHOPS

XANES and NEXAFS Spectroscopy: Theory and Applications

Boyan Boyanov
(North Carolina State University)

As x-ray absorption spectroscopy (XAS) matures as an analytical technique, more emphasis is placed on understanding and quantifying the fine structure in the near-edge region of the absorption spectrum. This year's workshop, which is the continuation of a series of XAS Workshops held at the NSLS Users' Meeting, reviewed recent progress in theoretical, acquisition, and analysis techniques, and facilities development at NSLS. More than 80 people attended the workshop.

The current state of the full multiple-scattering (FMS) technique for calculating XANES spectra was reviewed by Bruce Ravel from the National Institute of Standards and Technology (NIST). Bruce gave attendees an overview of the development goals and capabilities of FEFF8. Examples covered ranged from fairly routine simulations of the near-edge structure of K_2CrO_4, to difficult and time-consuming calculations for diamond. The factors affecting the precision and difficulty of the calculation, as well as the advantages and disadvantages of the FMS method in comparison to molecular orbital approaches, were discussed.

Stephen Wasserman from the Advanced Photon Source (APS/ANL) described the application of principle component analysis (PCA) for chemical speciation using XAS. Steve's presentation included many useful tips on practical issues, particularly on the difficult problem of deciding how many components describe the data in sufficient detail. The main advantages of the PCA method are that it provides an estimate of the number of distinct species observed in a series of measurements even when detailed analysis is not possible, and the ability to test whether a model compound is a constituent of the system being examined, without the need to know the other species present.

The present status of the Dow/NIST materials characterization facility at beamline U7A was reviewed by Daniel Fischer from NIST. The facility enables experimenters to perform new soft-x-ray materials science to study the chemical nature of diverse materials. Practical industrial problems currently being investigated include model catalyst systems, polymer surfaces and their interfaces, hard disk lubricant chemistry, self assembled monolayers, and high T_c superconducting tapes.

Stephen Urquhart from North Carolina State University (NCSU) discussed the use of XAS for the characterization of polymer systems. Stephen's talk explored the chemical information content of polymer NEXAFS spectra and the use of molecular models for the interpretation of the relationships between polymer structure and x-ray absorption spectra. He examined the significant perturbations of high-resolution spectra caused by electronic delocalization, and showed how the chemical sensitivity of NEXAFS can be utilized to perform chemical microanalysis of real-life polymers.

The final talk was given by Angelika Osanna from SUNY Stony Brook, who described the use of image stacks at beamline X1A to obtain images of sub-100 nm resolution of polymer and biological systems. Angelika gave a real-time demonstration of the acquisition and analysis software developed by Chris Jacobsen (also from Stony Brook), and described ongoing efforts to extend an existing database of amino acid spectra to oxygen and nitrogen edges.

The workshop concluded with a discussion by the participants of some outstanding issues faced by researchers in the field. The discussion covered a wide range of topics such as: the ability of self-consistent calculations to minimize the need of ad hoc adjustments

to important model parameters; the widespread need for reference libraries, particularly of polymers and amino acids; the limited applicability of the widely used "gaussian+arctan" deconvolution of near-edge structure, particularly in inorganic systems where effects are often very long-range in nature; factors that determine the temperature dependence of near-edge spectra (or the lack thereof); and the dependence of the detailed shape of soft x-ray near-edge spectra on the experimental setup, particularly when electron or fluorescence detection is used, and its implications for the ability to quantitatively analyze such spectra. ■

Infrared Synchrotron Radiation and Applications

Lawrence Carr
(Brookhaven National Laboratory, NSLS)

This workshop was held on May 18, 1998 at the NSLS and attended by approximately 60 people from more than 25 different institutions. Gwyn Williams (NSLS) began by reviewing the special characteristics of infrared synchrotron radiation (IRSR), the performance advantages of the NSLS VUV Ring, and the beamlines specifically built to utilize this radiation. Presently two IR beamlines are operational, and a third (for microspectroscopy) is very near completion. The remaining three IR beamlines have all delivered "first light" and beam distribution systems are being constructed. Wayne McKinney (Lawrence Berkeley National Laboratory) described the design and performance of their recently completed IR beamline at the ALS, along with their successful effort to reduce noise. A microspectrometer endstation is operational and already in use for the study of micro-organisms related to bioremediation. The high brightness of synchrotron radiation enables various measurement methods, such as ellipsometry, to be applied to small specimens. Alex Wittlin and collaborators from the Max Planck Institute (Stuttgart, Germany) have developed a custom ellipsometer for use in the far infrared, and have studied the "pseudo-gap" behavior in the c-axis response of small high-T_c oxide crystals. Grazing incidence reflection-absorption spectroscopy is another method that benefits from high brightness. Carol Hirschmugl (U. of Wisconsin - Milwaukee) reviewed the grazing incidence technique available at NSLS beamline U4IR and described two areas of active research; the study of absorbates on noble metals and thin oxide films on various transition metal surfaces. In the former case, additional insight has been gained into the interaction between various types of absorbates and the conduction electrons in the metal. Perhaps the best illustration of high brightness synchrotron infrared enabling an existing, wide-spread measurement method is microspectroscopy. John Reffner, former director of research at Spectra-Tech, Inc. reviewed microspectrometer instrumentation and pointed out areas where improvements were still available in conjunction with the synchrotron IR source. He remarked that a reduction in detector area could provide better signal-to-noise. One of the earliest examples of microsampling with infrared synchrotron radiation was the work by Rus Hemley and co-workers from the Geophysical Laboratory (Carnegie Institution of Washington). Their program makes use of an IR microscope-style optical system for probing materials inside ultra-high pressure diamond anvil cells. This group continues to investigate hydrogen at high pressure and low temperature for evidence of metallic behavior, as well as other "simple" materials such as ice, for which a new quantum ordered phase has been discovered. IR microsampling and chemical identification of extraterrestrial samples was described by George Flynn (SUNY at Plattsburgh). Interplanetary particles, collected from the Earth's upper atmosphere or extracted from meteorites found on the surface, are typically heterogeneous. Flynn's group uses two different NSLS

x-ray beamlines for elemental and some chemical mapping, as well as the infrared microspectrometer at U4IR for complete chemical identification. The latter allows the identification of both mineral phases and the presence of both simple and more complex (e.g. polycyclic aromatic hydrocarbons) organic compounds. Lisa Miller of the Albert Einstein College of Medicine presented two examples of how synchrotron infrared microspectroscopy can be used to the study biological cells and tissues. In her work on diseased bone (e.g. osteoarthritis), microtomed sections of bone tissue are examined for both protein and mineral content. By using an extrinsic photoconductive detector such as Ge:Cu, the microspectroscopy can be readily extended down to 400 cm^{-1}. Thus, bone mineralization can be tracked through both carbonate and phosphate vibrational features, and differences between normal and diseased bone are spatially resolved. The effect of typical cosmetic treatments on the properties of human hair were also shown. This work, by J.-L. Bantignies (ELF Atochem), shows how IR microspectroscopy can be used to image hair structures (e.g., the cortex and medulla) and detect variations in the water content as a function of hair treatment. The last two presentations addressed applications of the pulsed nature of synchrotron raiation to the field of time-resolved spectroscopy. Most synchrotron sources produce light in pulses shorter than 1ns in duration. David Tanner (U. of Florida) discussed the U12IR beamline at the NSLS and the synchronized Ti:sapphire laser system that can be used to perform pump-probe spectroscopy. A time resolution of better than 1ns has been achieved. Initial measurements on semiconductors and superconductors were described, as well as several candidate experimental systems. Richard Palmer (Duke U.) described an interesting time-resolved measurement system proposed for the Duke storage ring based FEL. Time-resolved spectroscopy could be performed in a manner similar to that being performed at the NSLS, namely pump-probe spectroscopy using a synchronized laser as the excitation source. ■